

Chapter 1

Process and Reaction Flavors: An Overview

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Maillard reaction, lipid oxidation, degradation of sugars, proteins, lipids, ribonucleotides, pigments and vitamins, and the interactions of degradation products are the chemical platform for generating many flavor compounds encountered in process and reaction flavors, flavorings and foods. The flavor industry is by far the largest user of knowledge from process and reaction flavor studies and has grown from approximately 2 billions, 20 years ago, to about 8 billion dollars in annual sales today. During the last few decades, much progress in the understanding and utilization of process flavors was made due to advances in chromatographic separation and computer-related technology, relentless investigation of a wide range of flavor precursors, regulation that met consumer safety concerns, and industry demand for better, complex and authentic products. This symposium was organized to shed some light on the current state of science in process and reaction flavors, and to report recent significant findings.

Flavor Industry and Flavor Technology

The global market for the flavor and fragrance industry is estimated at more than 15 billion dollars today (1,2). Approximately 525 companies contribute to this market. About half of the 15.1 billion dollar worldwide flavor & fragrance sales is flavor, which splits between dairy (14%), savory (23%), beverages (31%) and other (32%). The market has almost quadrupled over the last 20 years (figure 1). However, the last few years registered slow growth, which has resulted in mergers and acquisitions, downsizing and cutback on innovation initiatives.

Restructuring has lead to 10 companies controlling about 2/3 of the market. James Giese (3) recently reported that in 1995, 10 companies made up 59% of the market share, but by 2000, 8 companies had 71% of the market share. The drawback of all these mergers and acquisitions is the elimination of technical positions and the reduction of R&D budgets. A recent report of the number of patents in process and reaction flavors filed during the last quarter of century (4) indicates a steady increase from 1980 to 2000, then a steep decline thereafter (figure 1), which may be due to a significant reduction in R&D resources. The trends in patent generation also find good correlation with flavor sales. Ironically, the flavor industry is by far the largest user of knowledge from flavor research, and much progress in the understanding and utilization of process flavors was made due to advances in chromatographic separation and computer-related technology, relentless investigation of a wide range of flavor precursors, regulation that meets consumer safety concerns, and industry demand for better, complex and authentic products. This offering provides background information on the state of knowledge in the aforementioned areas and concludes on key research gaps.

Advances in Chromatographic Separation and Computer-Related Technology

Prior to gas chromatograph (GC), the characterization of unknown volatile flavor compounds was a tedious task. Great strides in flavors research have been made since its invention by James and Martin in 1952. Earlier GC column were packed columns, and by 1960, only 500 flavor compounds had been identified in

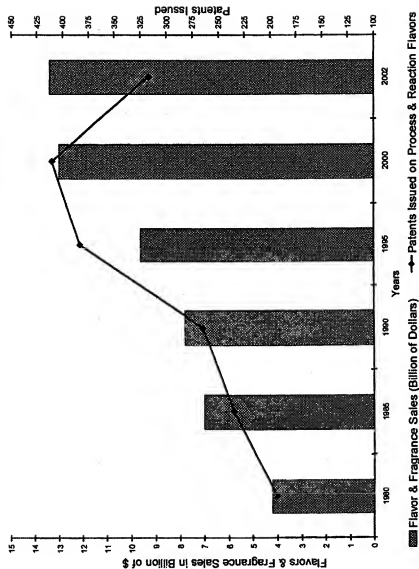


Figure 1. Flavor & Fragrance Sales (1,2), and Process & Reaction Flavor Patents Issued (4).

foods. The development of high resolution glass capillary columns and tandem gas chromatography/mass spectrometer techniques in the mid 1960's has made possible the identification of tremendous number of flavor constituents. Improvement in GC detectors hardware and progress in computer technologies, have leveraged the magnitude of sensitivity obtainable in the identification of flavor compounds. Improvement in flavor isolation methods was also key contributor to the increased sensitivity. Flavors compounds must be isolated from the complex matrix of foods material before chromatographic analyses. Earlier methods of isolation were sometimes fraught with pitfalls and difficulties, and often sources of artifact formation. Although tremendous progress has been made in terms of limiting artifact formation, real-time aroma release measurement in the mouth, developed by Taylor and co-workers, is a significant development in flavor research (5).

As gas chromatography evolved in sophistication, progress was made in the characterization of flavor compounds and in the elucidation of their chemical pathways. Initial researches focused on the identification of long list of flavor compounds, which has resulted in the identification of more than 7,000 aroma compounds in foods (5). Because, it was impossible to recreate food flavors from the laundry lists of chemicals, earlier attempts were made to determine character impact compounds. Except for few foods, the flavors of many foods are not determined by character impact compounds, rather results from a combination of several key flavor constituents. Today, there are several established methods (CHARM, AEDA, Odor Unit Value) used in the determination of key aroma constituents in foods.

Regulation That Meets Consumer Safety Concerns

Under FEMA (Flavor and Extract Manufacturer's Association) and IOFI (International Organization of Flavor Industry), the flavor industry established an independent expert panel for the review of flavor ingredient safety, certainly because of consumers' awareness and concerns. FEMA introduced a GRAS list of allowed substances in 1965, and has added nearly 2000 compounds since then (6). IOFI is in the process of establishing a list of flavor ingredients it considers safe for use in foods.

FEMA was founded in 1909, and is the sole national association of the flavor industry. FEMA assists in the enactment and enforcement of laws which deal with the rights of flavor manufacturers and consumers, and in the processes which assure its members a supply of safe flavor materials. FEMA's most important activities include safety evaluation of flavor ingredients, protection of member company's intellectual property, establishment of GRAS list,

responding to government regulations affecting members, participating in the development and review of flavor ingredient specifications and international regulations of method of safety evaluation, organizing annual membership meeting and monitoring and addressing issues related to flavor labeling (7).

Industry Demand for Better, Complex and Authentic Products

Consumers' demand for authentic and home-like meal flavors prompted the flavor industry to hire corporate chefs to work side-by-side with flavor chemists in the process of flavor development. Flavors from traditional cooking techniques, that take several hours to several days to develop desired profiles, are now matched by flavor chemists. In this process, the corporate chef designs a gold standard food product, and the flavor chemist provides a match to the flavor of the gold standard.

Study of Flavor Precursors

Many compounds encountered in process and reaction flavors derive from Maillard reactions, lipid oxidation, degradation of sugars, proteins, lipids, ribonucleotides, pigments and vitamins, and from the interactions of degradation products. The Maillard reaction is actually a complex group of hundreds of possible reactions. In foodstuffs, Maillard reaction or nonenzymatic browning reaction is responsible for changes in aroma, taste, color and nutritive value during processing and storage. The Maillard reaction in foods has been subject to several reviews (8,9,10,11). An important reaction associated with Maillard reaction is Strecker degradation which involves oxidative deamination and decarboxylation of amino acids in the presence of dicarbonyls. Strecker degradation leads to the formation of aldehydes containing one fewer carbon atom than the original amino acids, and alpha-amino ketones precursors of pyrazines (12). Hydrogen sulfide, ammonia, and acetaldehyde are also formed from the breakdown of mercaptoiminol Strecker intermediate from cysteine specific reaction (12,13).

Historical Perspective

The earliest reported scientific studies of Maillard reactions were by Dr. Louis Camille Maillard in figure 2 (14) who, in an attempt to determine the biological synthesis of proteins, heated concentrated solutions of D-glucose and amino

acids, and observed a gradual darkening and frothing accompanied by odors reminiscent of the baking of bread and roasting of animal or vegetable products. The elucidation of the chemical pathways in Maillard reaction started with the work of John Edward Hodge (figure 3), of USDA Northern Regional Research Center in Peoria, IL, USA, on the "chemistry of browning reactions". Hodge gained much attention in 1979 among carbohydrate chemists when his 1953 article on "Dehydrated Foods, Chemistry of Browning Reactions in Model Systems", *Journal of Agricultural and Food Chemistry*, volume 1, issue 15, page 928, was named a "Citation Classic" by the Science Citation Index. It is interesting to note that the mechanism proposed by Hodge in 1953 still provides the basis for our understanding of the early stages of Maillard reactions (12).

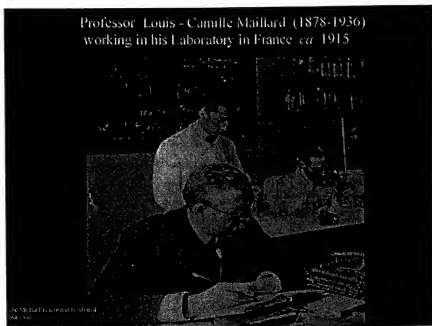


Figure 2. Photograph of Professor Louis-Camille Maillard. Courtesy of ACS Symposium Series 215.

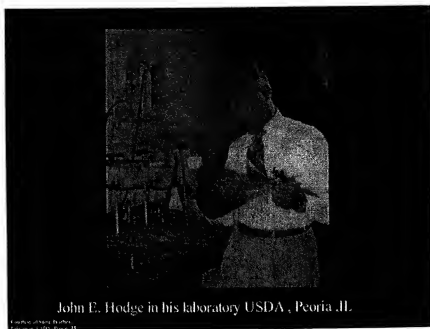


Figure 3. Photograph of Professor John E. Hodge. Courtesy of Steve Prather, Librarian, USDA, Peoria, IL.

The Maillard Reaction

The first step of Maillard reaction series involves Schiff base formation between the carbonyl group of a reducing sugar and the free amino group of an amino acid, peptide or protein. These Schiff bases (also known as N-glucosylamines or N-fructosylamines) can rearrange to form 1-amino-1-deoxy-2-ketose (Amadori compounds) and 1-amino-2-deoxy-2-aldose (Heyns compounds). Amadori and Heyns compounds can undergo dehydration to form furfural (from pentose) or hydroxymethyl furfural (from hexose), or can rearrange into 1-deoxyglycosones or 3-deoxyglycosones (reactive reductones and dehydroreductones). The latter can undergo retro-aldolization reaction to form α -dicarbonyls (diacetyl, pyruvaldehyde, acetoin,) which subsequently interact with ammonia and hydrogen sulfide to produce important flavor compounds. Potent odorants formed from Maillard reactions include 3-Methylbutanal, 2,3-butanedione, methional, phenylacetaldehyde, 2-furfurylthiol, 2-ethyl-3,5-methylpyrazine, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, etc. Major classes of Maillard reaction aroma compounds are Strecker aldehydes, and more importantly heterocyclic compounds containing nitrogen, sulfur, oxygen, and combination of these atoms. Maillard reaction products can be specific to the type of amino acids used in the reaction system.

Maillard Specific Reactions

Cystein-specific Maillard reaction include mercaptoacetaldehyde, mercaptopropionic acid and derivatives of thiane, thiolane, thiazine, and thiophene. Proline-specific compounds are pyrrolidins, piperidins, pyrrolizines and azepines. Of methionine-specific compounds, heterocyclic compounds containing a methylthioethyl or methylthiopropyl side chain such as 2-(2-methylthioethyl)-4,5-dimethyloxazole and 2-(3-methylthiopropyl)-5,6-dimethylpyrazine are most interesting. Additionally, methional, methanethiol and 2-propenal are important methionine-specific compounds. Methional can decompose into methanethiol, dimethyl sulfide, dimethyl disulfide and propenal. 3-Methyl-2(1H)-pyrazinone is specific product formed from the reaction of asparagine and glucose. The reaction of glucose with histidine led to the formation of amino acid specific compounds 2-acetyl- and 2-propionyl-pyrido[3,4-d]imidazole along with their tetrahydropyrido derivatives (15).

Thiamine Degradation

The thermal degradation of thiamine is very important in process flavors and has been investigated by several authors (16,17,18,19). Aqueous system at pH 2.3/135 C/30 min generated more decomposition products (carbonyls, furanoids, thiophenoids, thiazoles and aliphatic sulfur compounds) than propane-1,2-diol system (17). Reineccius and Liardon (18) studied the degradation products from thiamine at lower temperatures (40, 60, and 90C) at pH 5, 7 and 9, respectively. At pH 5 and 7, the meaty compounds 2-methyl-furan-3-thiol and bis(2-methyl-3-furyl) disulfide with various thiophenes were the major reaction products, while at pH 9 the meaty compounds were not significant and the thiophenes predominated. Additional thiamine degradation products reported to be meaty include 3-mercapto-2-pentanone, 2-methyl-4,5-dihydro-furanthiol, 2-methyltetrahydrofuran-3-thiol, 4,5-dimethyl thiazole and 2,5-dimethylfuran-3-thiol. To date, the degradation products 2-methyl-furan-3-thiol, bis(2-methyl-3-furyl) disulfide, and thiazole have been found in beef. The degradation product 5-hydroxy-3-mercapto-2-pentanone is key intermediate in the formation of a number of furanthiols and thiophenes.

Lipid Oxidation

Lipid oxidation/degradation of saturated and unsaturated fatty acids leads to the formation of many aliphatic hydrocarbons, alcohols, aldehydes, ketones, acids, lactones, 2-alkylfurans and esters. Other lipid-derived flavors are the benzenoids

benzaldehyde, benzoic acid, alkylbenzenes and naphthalene. Lipid oxidation starts in raw beef and continues during cooking. Mottram et al. (20, 21) and later MacLeod (22) demonstrated that the intramuscular lipids (not the adipose tissues) are responsible for the formation of most of the lipid-derived volatiles.

Non-volatile precursors of process flavor aromas are formed upon hydrolysis of substrate biopolymers, and include peptides, amino acids, nucleotides, vitamins, and reducing sugars. These compounds contribute to sweet, salty, sour, bitter and umami sensations. While the sugars contribute to sweet taste, and the acid to sour taste exclusively, the amino acids and simple peptides elicit all the 5 primary taste sensations. Most of the aroma-active compounds encountered in process flavors are generated upon heating from non-volatile precursors (23) as an effect of lipid oxidation and degradation, and from degradation and interactions of sugars, amino acids, ribonucleotides, proteins, pigments and vitamins (figure 4). Over 10,000 flavor compounds have been identified and range from the simple hydrocarbons, aldehydes, ketones, alcohols, carboxylic acids, esters, ethers, to the more complex lactones, furans, pyrroles, pyridines, pyrazines, thiophenes, thiazoles, oxazoles, and other sulfur and nitrogen-containing substances.

Meat Flavors

Raw meat has only a weak sweet aroma resembling serum, and a salty, metallic, bloody taste. However, it is a rich reservoir of compounds with taste properties and aroma precursors (24). Each meat has a distinct flavor characteristic. The flavors of distinct meat species or species-specific flavors are often carried by the lipid fraction (25). For example 4-methyloctanoic and 4-methylnonanoic acids are specific to mutton while (E,E)-2,4-decadienal is specific to poultry meat. 12-Methyltridecanal has been identified as species-specific odorant in stewed beef, and is responsible for the tallowy and beef-like smell (26). The distinctive pork-like or piggy flavor noticeable in lard has in part been attributed to p-cresol and isovaleric acid (27,28,29).

The major precursors in meat flavors are the water-soluble components such as carbohydrates, nucleotides, thiamine, peptides, amino acids, and the lipids, and Maillard reaction and lipid oxidation are the main reactions that convert these precursors in aroma volatiles. The thermal decomposition of amino acids and peptides, and the caramelization of sugars normally require temperatures over 150C for aroma generation. Such temperatures are higher than those normally encountered in meat cooking. During cooking of meat, thermal oxidation of lipids results in the formation of many volatile compounds. The oxidative breakdown of acyl lipids involve a free radical mechanism and the formation of

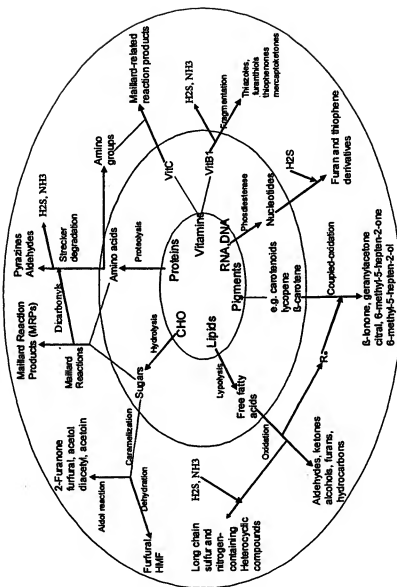


Figure 4. Wheel of Chemical Reactions Important to Flavor Formation (23)

hydroperoxides which subsequently decompose into aroma compounds. Phospholipids contain high amount of unsaturated fatty acids, and are major contributors to lipid oxidation products (13).

Poultry Flavor

In poultry meat, Maillard reactions and lipid oxidation are major sources of volatile flavor compounds (30). The meaty flavor of chicken broth has been found to be due to 2-methyl-3-furanthiol (31). This compound has also been recognized as a character impact compound in the aroma of cooked beef (30,31). However, a major difference between beef and chicken is that bis(2-methyl-3-furyl) disulfide, the oxidation product of 2-methyl-3-furanthiol and responsible for a meaty note, and methional which is responsible for a cooked potato attribute, predominate in beef whereas volatiles from the oxidation of unsaturated lipids, in particular E,E-2,4-decadienal possessing a fatty taste, and gamma-dodecalactone possessing a tallowy, fruity taste, prevail in chicken (23). Schroll and co-workers (32) found that the most abundant aldehydes in chicken flavor are hexanal and 2,4-decadienal, and that the enzymatic hydrolysis of chicken with papain increased the concentration of 2,4-decadienal from 5.2 to 13.7 mg/Kg. Hexanal and 2,4-decadienal are primary oxidation products of linoleic acid. The autooxidation of linoleate generates 9- and 13-hydroperoxides. Cleavage of 13-hydroperoxide leads to hexanal, and the breakdown of 9-hydroperoxide generates 2,4-decadienal (33). The 2,4-decadienal is a more potent odorant with threshold value of 0.00007 mg/kg compared to hexanal (0.0045 mg/kg). The major volatile compounds present in poultry meat include hexanal, 3-octen-2-one, 1-pentanol, pentanal, heptanal, octanal, 1-heptanol, 1-octanol, 1-octen-3-ol. No pyrazines were found in chicken broth, but in fried or roasted chicken, indicating that low moisture and high temperature favor the generation of pyrazines.

Pork Flavor

Lipid-derived volatile compounds dominate the flavor profile of pork cooked at temperatures below 100°C. The large numbers of heterocyclic compounds reported in the aroma volatiles of pork are associated with roasted meat rather than boiled meat where the temperature does not exceed 100°C (34,35). Of the volatiles produced by lipid oxidation, aldehydes are the most significant flavor compounds (35,36). Octanal, nonanal, and 2-undecenal are oxidation products from oleic acid, and hexanal, 2-nonenal, and 2,4-decadienal are major volatile oxidation products of linoleic acid.

Beef Flavor

It is estimated that cooked beef has 880 volatiles (37). Of these volatile compounds, only 25 have been reported to have meat odor (38,39). Aroma components are formed from non-volatile precursors on cooking as a result of lipid oxidation and Maillard reaction and degradation of thiamin, and inter-reactions of degradation products from sugars, amino acids, ribonucleotides and proteins. Meaty compounds form preferably at pH 2.2 and 5.1 rather than pH 7.1 (40). Several compounds reported to be meaty were generated at pH 2.2 and the pH of meat (pH 5.5). 4-Hydroxy-5-methyl-3(2H) furanone and 2,5-dimethyl-4-hydroxy-3(2H) furanone have been isolated from beef (but not from any other meats) and are important aroma precursors (23). Natural precursors of 4-hydroxy-5-methyl-3(2H) furanone in beef are ribose-5-phosphate and can be formed upon heating at 100C for 2.5 hours at pH 5.5 (23). Ribose-5-phosphate can be obtained from nucleotide by heating at 60C or during autolysis in muscle. Precursors of 2,5-dimethyl-4-hydroxy-3(2H) furanone are optimum at pH 4 and decomposes rapidly with temperature (41, 23). These furanone react readily with hydrogen sulfide to generate a host of heterocyclic compounds containing oxygen and/or sulfur atoms. 2-Alkyl-(2H)-thiapyran and 2-alkyl-thiophene were found in the volatiles of cooked beef and lamb trimmed fat cooked at 140C for 30 min (42). 2-Alkyl-(2H)-thiapyrans were formed when 2,4-decadienal was reacted with H₂S at 140C for 30 min. Grosch and coworkers have developed a screening protocol to select beef aroma components of high sensory significance (31).

Lipid oxidation starts in raw beef and continues during cooking. Mottran et al. (21) demonstrated that the intramuscular lipids (not the adipose tissues) are responsible for the formation of most of the lipid-derived volatiles. Intramuscular lipids consist of marbling fat made primarily of triglycerols and structural or membrane lipids made of phospholipids. The phospholipids contain relatively high amount of unsaturated fatty acids more prone to oxidation. In beef, the intramuscular tissue phospholipids are sufficient in imparting a full meaty aroma (22).

Sheepmeat

Unlike the taboos that apply to beef (Hindu) and pork (Moslem, Jewish), there are no religious or cultural taboos on eating sheepmeat. In spite of this fact, consumption of sheepmeat remains low because of objectionable odor and waxy mouthfeel upon ingestion due to high melting point fat (46). The objectionable goaty and muttony odors have been attributed to the branched chain fatty acids 4-methyloctanoic, 4-ethyloctanoic and 4-methylnonanoic acids (47,24).

Hydrolysis of triglycerides or other precursors accounted for most of these acids. Ha and Lindsay (48) proposed that alkylphenols contributed to sheepmeat odor. Subsequently, Young et al., (49) reported that 4-methylphenol was correlated with animal odor. It has been reported that mutton aromas contain higher concentrations of 3,5-dimethyl-1,2,4-trithiolane and thialdine (2,4,6-trimethylperhydro-1,3,5-dithiazine) as compared to those of others species. Other sulfur-containing compounds were also found in higher amount and this observation was attributed to the high content of sulfur-containing amino acids in mutton compared with those in beef and pork (24). Kunsman and Raley (50) found that the depot fat tissues of lamb produced considerably more hydrogen sulfide than those of beef. In sheepmeat, glutathione is the sulfur precursor implicated in hydrogen sulfide formation (51).

Seafood Flavors

The flavor of fish and seafoods is composed of taste-active low molecular-weight extractives and aroma-active compounds. The taste-active compounds are more abundant in the tissues of mollusks and crustaceans than fish. The most important non-volatile taste components are free amino acids, nucleotides, inorganic salts and quaternary ammonia bases. Alcohols, aldehydes, ketones, furans, nitrogen-containing compounds, sulfur-containing compounds, hydrocarbons, esters and phenols are the most important volatiles in shellfish. Alkyl pyrazines and sulfur-containing compounds are important contributors to the cooked aroma of crustaceans. Furans, pyrazines, and Lactones have been found in heat-treated seafoods. Dimethyl disulfide, dimethyl trisulfide, heterocyclic sulfur-containing compounds (alkylthiophenes) have been found in most thermally treated crustaceans like prawn, crab, oyster, crayfish and shrimp (52).

The aromas associated with very fresh fish are usually mild, delicate and fresh (53,54), and generally described as green (hexanal), melon-like ((E,Z)-3,6-nonadienal), iodine-like (bromophenols). Fresh fish and seafood aromas are due to volatile carbonyls and derive from lipoxygenase catalyzed oxidation of polyunsaturated fatty acids. The oxidation of Eicosapentaenoic acid (C20:5) leads to C5 to C9 alcohols, aldehydes, ketones and hydrocarbons. The formation of methyl mercaptan, dimethyl sulfide and dimethyl disulfide in fresh fish at the time of harvest has been reported by Shiomi et al. (55). Although these compounds are usually associated with fish deterioration, they contribute to the fresh aroma character at low concentrations. For instance, dimethyl sulfide is

known to provide a pleasant seashore-like smell while dimethyl disulfide gives a pleasant crab-like aroma at concentrations less than 100 ppb. Low concentrations of bromophenols may be responsible for the desirable brine-like or sea-like aroma associated with salt-water fish (56).

Fish deterioration arise from the reduction of trimethylamine oxide (TMAO), autoxidation, through contamination from environmentally derived flavors, such as Geosmin and 2-methylisoborneol, and processing. TMAO has no odor whereas TMA is described as old fish or fish house-like. Autoxidation of polyunsaturated fatty acids eicosapentaenoic and docosahexanoic acids forms 2,4,7-decatrinal and other aldehydes. 2,4,7-Decatrinal is associated with fishy, cod liver oil-like aromas. Geosmin and 2-methylisoborneol are produced by microorganisms in water, and elicit musty or earthy flavors. Alkyl- and thiophenols from industrial waste are responsible for offensive taint odors in fish.

Hydrolyzed Vegetable Proteins

Hydrolyzed vegetable proteins (HVP) have been used to impart savory and meaty flavor to various foods. They are known to enhance and intensify naturally occurring savory flavors, and generally round off and balance the savory characteristics of the food material. Unfortunately, they lose attractiveness as food ingredient because of the high content of salt, monosodium glutamate, monochloropropanols and dichloropropanols. The propanols are known carcinogens, and this has made food processors limit the use of HVP in new product development. Furthermore, at temperatures above 200C, they become unstable and lose their typical flavor with the development of caramelized and salty taste on prolonged heating.

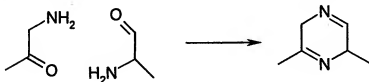
Wheat gluten, corn gluten, defatted soy flour, defatted peanut flour, defatted cotton seed flour are sources of proteins for HVP manufacturing. A typical HVP process calls for hydrolysis with HCL for 11 hours at 212F or 1.5 hours at 250F. The process mixture is a concentrate containing 23% water, 32% HCL (at 35%), 13% NaOH, and 32% flavor solids rich in proteinaceous material (57). Under the conditions used in hydrolysis, the amino acids from proteins react with carbohydrates through the well-known Maillard reactions to produce meaty flavors. The hydrolysate is neutralized with NaOH to pH 4.8 to 6.0. To meet customer demand, salt, MSG, caramel color, and other food additives are often added to HVP.

Yeast Extracts and Autolysates

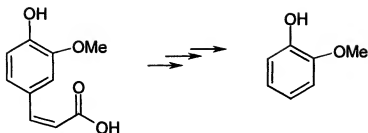
Typical flavor notes that yeast extracts and autolysates (YEA) impart to foods are cheesy, meaty or savory. YEA finds application in such products as meats, meat dishes, soups, bouillions, sauces, gravies, cheese, barbecue, salad dressings, seasoning salts, spreads, etc. Aside from flavor enhancement, yeast products are used as texturizers, stabilizers and thickeners. Yeast products are also well known for their nutritional benefits, and are incorporated into many foods as ingredients for nutritional fortification due to their relatively high content of proteins, vitamins (B1, B2 and nicotinic acid) and minerals (58). YEA are products of self-digestion or autolysis of yeast cells (baker's, torula, brewer's). During the autolytic process, yeast endogenous enzymes hydrolyze yeast proteins, nucleic acids and carbohydrates to their monomer units with taste properties. Different savory and meaty notes are developed by varying the autolysis conditions. Autolysis results in a slurry called yeast autolysate. The removal of cell walls and bitter tasting compounds from the slurry yields a liquid known as yeast extract. The organoleptically desired odors of yeast extracts are predominantly developed during heat processing by complex series of reaction involving Maillard reactions, lipid oxidation, and thermal degradation of fat, sugars, amino acids, thiamin, nucleotides, etc. Heterocyclic flavor compounds such as thiazoles, pyrroles, pyrazines, and trithiones, formed during processing, have the greatest impact on final flavor (59).

Coffee Flavors

Coffee flavors form during roasting from dicarbonyl compounds which derive from carbohydrates. The thermal degradation of hexoses is thought to be the precursors of furanones like HDMF. The presence of alkylpyrazines affords the characteristic roast notes. These pyrazines are formed through Strecker degradation and the condensation of the resulting Strecker products (60).



The astringency and the mouth feel of coffee is partly attributed to the presence of phenols which are thought to be formed by the degradation of feruloyl quinic acid (61).



Thiols are another key group of odor compounds in coffee, these are formed due to Strecker degradation of amino acids like methionine to give methional and the reaction of H₂S (formed by the degradation of Cysteine) with furaldehydes, namely the formation of 2-furfurylthiol (62).

Coffee flavor has been subject of several studies (63, 64, 65, 66, 67, 68). Over 800 flavor compounds have been identified in coffee, and some of those important to flavor are listed in table I. There is evidence that coffee flavor is unstable. Kumazu and Masuda (66) reported that the sulfur compounds 2-furfurylthiol, methional, 3-mercapto-3-methylbutyl formate decreased in coffee brew during heating, while methanethiol, acetic acid, 3-methylbutanoic acid, 2-furfuryl methyl disulfide and 4-hydroxy-2,5-dimethyl-3(2H) furanone increased. Melanoidins in coffee brew are also involved in the loss of 2-furfurylthiol. These observations concur with those made by Hoffmann & Schieberle (64), and Hoffmann et al (63). The loss of 2-furfurylthiol through a Fenton-type reaction system was also investigated by Blank et al (69), with up to 90% 2-Furfurylthiol readily decompose to difurfuryl disulfide and trisulfide upon heating at 37°C for 1 hour.

Chocolate Flavors

Cocoa aroma is crucially dependent on harvesting, fermentation, drying and roasting conditions. The fresh beans have the taste and aroma of vinegar. During roasting, lipid oxidation, Maillard reaction and Strecker degradation processes lead to aroma formation. Counet et al (70) reported that via Maillard reactions, cocoa roasting converts flavor precursors formed during fermentation to 2 main classes of odorants pyrazines and aldehydes. More than 600 flavor compounds have been identified in cocoa and cocoa products (70, 71). The most important odorants of cocoa mass, determined by AEDA, have been reported by Belitz and Grosch (72). Amino acids released from fermentation served as precursors to 3-methylbutanal (malty), phenylacetaldehyde (honey-like), 2-methyl-3(methyldithio)furan (cooked meat-like), 2-Ethyl-3,5-dimethylpyrazine (earthy,

roasted) and 2,3-Diethyl-5-methylpyrazine (earthy roasted) during roasting. These authors (72) also reported the occurrence of ethyl 2-methylbutanoate (fruity), hexanal (green), 2-methoxy-3-isopropylpyrazine (peasy, earthy), E-2-octenal (tallowy), E-2-nonenal (fatty, waxy), Z-4-heptanal (biscuit-like), delta-octalactone and delta-decalactone (sweet coconut like) among the odorants of cocoa mass. Counet and co-workers (70) revealed the presence of 33 potent odorants in the neutral/basic fraction of dark chocolate by AEDA. Three of them, 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal had strong chocolate odor. 2,3-Dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine, dimethylethylpyrazine, diethylmethylpyrazine, and furfurylpyrrole were characterized as possessing cocoa, nutty, coffee notes.

Bread Flavors

Although more than 280 compounds have been identified in the volatile fraction of wheat bread, only a small number is responsible for the flavor notes in the crust and the crumb. Schieberle and Grosch (73) used aroma extract dilution analysis (AEDA) to select 32 odorants in wheat. Among the odorants, 2-acetylpyrroline (roasty, bread crust-like) was the most potent aroma, followed by E-2-nonenal (green, tallowy), 3-methylbutanal (malty, nutty), diacetyl (buttery) and Z-2-nonenal (green, fatty).

Bread flavors compounds 2-acetylpyrroline and 6-acetyl-1,2,3,4-tetrahydropyridine (cracker-like) derive from Maillard reactions. Maillard reaction products maltol and isomaltol contribute to the freshness of baked bread. Kirchoff and Schieberle (74) reported that the typical flavor of bread is formed as a result of enzymatic reactions occurring during dough fermentation by yeasts and/or lactic acid bacteria followed by thermal reactions during baking. The authors also found that 3-methylbutanal, E-2-nonenal, acetic acid, 2,4-decadienal, hexanal, phenylacetaldehyde, methional, vanillin, 2,3-butanedione, 3-OH-4,5-dimethyl-2(5H) furanone and 2,3-methylbutanoic acid were important contributors to the flavor of sourdough bread crumb.

Flavor Stability

One challenge facing the flavor industry today deals with the stability of process/reaction flavors to heat, UV-light, oxidation, binding to food matrices, diffusion and interactions with the environment in which they find application. Seeventer et al. (75) studied the stability of thiols formed from model system ribose/cystein, and reported that 2-methyl-3-furanthiol, 2-furfurylthiol, 2-mercapto-3-butanone and furanone decreased during storage. In brewed coffee,

Table 1 Most important chemicals responsible for the coffee flavor notes.

Compounds	Descriptors	Ethiopian Arabica (68) (CHARM- Analyst)	Columbian Arabica (68) (AEDA)	Indonesian Robusta (72) (Aroma Value)
4-Ethyl-2-methoxyphenol (4-vinylgualacol)	phenolic	490	256	8900
4-Hydroxy-2,5-dimethyl- 3(2H)-furanone (furanol)	sweet-caramel	410	256	5700
3-Methyl-2-buten-1-thiol	smoke-roast	360	16	28000
Beta-Damascenone	sweet-fruity	340	32	270000
2,3-butanedione (diacetyl)	buttery	340	6	3200
2-Furfurylthiol	smoke-roast	320	64	170000
Methional	soy sauce	310		
3-Methylbutyric acid	acidic	280		
2- and 3-Methylbutanals	buttery	240		
2-Methyl-3-furanthiol	nuty-roast	230	16	
2-Ethyl-3,5-dimethylpyrazine	nuty-roast	230	64	5900
2-Methoxyphenol (gualacol)	phenolic	210	128	11000
2-Methoxy-3-(2- methylpropyl)pyrazine	green-earth	200		
3-Mercapto-3-methylbutyl formate	green-black	190	64	33000
2,3-Pentanedione	currant	180	16	660
6,7-Dihydro-5-methyl-5H- cyclopentapyrazine	nuty-roast	170		
2-Ethyl-4-hydroxy-5-methyl- 3(2H)-furanone (homofluranol)	sweet-caramel	170	128	12000

2,3-Diethyl-5-methylpyrazine	nutty-roast	120	64	3400
E-2-Nonenal	buttery	39		
Unknown	sweet-caramel	30	16	
Unknown	sulfurous, burnt		64	360
Unknown	earthy		256	640
4-Ethyl-guaiacol			32	32
Vanillin			64	
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon)	caramelic, curry, seasoning-like		32	11
5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone (alhexon)				
Isobutyl-2-methoxy-pyrazine				3000

decrease in amount of 2-furfurylthiol, methional, and 3-mercapto-3-methylbutyl formate was observed after heating, and has been attributed to interactions with melanoidins (63,64,66). The loss of 2-furfurylthiol was linked to Fenton-type oxidation upon heating at 37°C for 1 hour (69).

Summary

Considerable progress has been made in characterization of process flavors, study of flavor precursors, and flavor regulation. Nevertheless, the growing demand for authentic and ethnic foods in the western world calls for renewed efforts in process and reaction flavors. Moreover, although work is underway to elucidate structure and properties of taste-active compounds in process and reaction flavors, more work remain to be done. This symposium reports recent significant findings in process and reaction flavors.

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